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Excitons in C_{60} studied by temperature-dependent optical second-harmonic generation

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The electric-dipole-forbidden $^1T_{1g}$ excitonic state of solid C_{60} at $\hbar\omega$=1.81 eV can be probed with a second-harmonic generation (SHG) experiment. We show that the SHG line shape depends strongly on the degree of rotational order. We observe a splitting into two peaks below the rotational ordering phase-transition temperature of 260 K. The origin of this splitting is discussed in terms of a possible Jahn-Teller effect, a possible Davydov splitting due to the four molecules per unit cell in the low-temperature phase, and a mixing of the nearly degenerate $^1T_{1g}$ and ^1G_g free molecule states because of the lower symmetry in the solid. The exciton band structure is calculated with a charge-transfer-mediated propagation mechanism as suggested by Lof *et al.*[2] and with one-electron (-hole) transfer integrals determined from band-structure calculations. Comparison with our experimental SHG data leads to a reasonable agreement and shows that a mixing of $^1T_{1g}$ and ^1G_g states may explain the splitting at low temperature.

I. INTRODUCTION

In spite of the large amount of research done on C_{60} and its compounds since its discovery,[1] the electronic structure and the importance of solid-state band-structure effects remain controversial. Solid C_{60} seems to exhibit a dualistic behavior. On one hand, it behaves like a molecular crystal in which the molecular properties (like the vibrational states and electronic excitations) are only weakly perturbed by the crystal symmetry, but on the other hand, it behaves like a semiconductor, with a moderate [2.3 – 2.6 eV (Refs. 2 and 3)] band gap, which can be electron doped, resulting in low-energy impurity states and bandwidths of about 0.6 eV.[4,5] Also quite different from typical molecular crystals is that C_{60} forms ionic compounds, which in some cases exhibit metallic and even superconducting[6] behavior, clearly demonstrating the importance of one-electron band formation. With regard to the properties of these compounds, they are reminiscent of the charge-transfer type of molecular solids like the much-studied tetracyanoquinodimethane (TCNQ) salts except that the C_{60} compounds usually show three-dimensional (3D) behavior rather than the one- or two-dimensional behavior exhibited by the charge-transfer molecular solids. This, obviously, is due to the spherical rather than linear or planar structure of the molecule. In this paper we present evidence that in pure C_{60} the excitons also exhibit this dualistic behavior. The energies of the excitonic states are close to those of the gas-phase molecule emphasizing the molecular characteristics, but the propagation of the exciton results in abnormally large excitonic bandwidths and mixings of different multiplets for a molecular solid. This can be explained within a one- and two-particle band-structure theory.

It is well established that the strong delocalization of the p_π-electron network (as is also the case on a C_{60} molecule) can result in strong nonlinear optical effects.[7] Koopmans *et al.*[8,9] have shown that the second-harmonic (SH) signal is very strong due to a double resonance if the primary energy is tuned to the $^1T_{1g}$ excitonic state at 1.81 eV. This provides a possibility to study the excitons inside the electronic band gap, in particular the exciton bandwidth, the band splitting due to crystallographic phase transitions, and the mixing of multiplets due to the crystal symmetry. To facilitate this study we have developed a theory for the exciton splittings and dispersions based on the molecular multiplet splittings and solid-state effects arising from a charge-transfer mechanism for the exciton propagation.[2,10] The one-electron (-hole) hopping integrals required for this are obtained from a tight-binding fit to the local-density approximation (LDA) band structure of C_{60} as given by Satpathy *et al.*[11] We show that reasonable agreement can be obtained with the experimental SH line shape with only one adjustable parameter, namely, the $^1T_{1g}$ - ^1G_g molecular multiplet splitting.

II. EXPERIMENT

C_{60} with a purity better than 99.99% was evaporated from a Knudsen cell onto a substrate at UHV pressures below 4×10^{-9} mbar. As substrates we used fused quartz or, at low temperature, MgO, a good thermal conductor.

For the SH experiments a Nd:YAG laser was used to pump a dye laser, producing 7 ns pulses with an energy of approximately 6 mJ/pulse and a repetition rate of 10 Hz. The fundamental frequency was scanned in the range $\hbar\omega$= 1.7–2.0 eV. The SH intensities were calibrated by using a reference quartz crystal in a transmission geometry, carefully tuned to a Maker fringe optimum by fine tuning the frequency, and corrected for changes of the

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coherence length in the quartz crystal as a function of the photon energy. All SH experiments are performed at a fixed angle of incidence (45° to the surface normal) and the specular reflected SH signal was detected.

The second-harmonic generation (SHG) of thin C_{60} films exhibit complicated thickness- (and through the dispersion also frequency-) dependent interference phenomena. We showed earlier[8] that for a mixed $m_{in}-p_{out}$ polarization (m-p) combination (mixed means 50% p and 50% s polarized light), the SH interference pattern exhibits a broad minimum for C_{60} film thicknesses of around 250 nm. Therefore we chose an m-p polarization combination and a thickness of 250 nm for the measurements presented in this paper, so that dispersive interference effects can be neglected.

The temperature-dependent SHG experiments were performed using a He-flow cryostat (4 – 500 K). The temperature was measured with a thermocouple glued to the substrate. Possible effects of heating during the laser pulse were examined by varying the laser power. We found that below 100 K the temperature during the laser pulse was about 20–30 K higher than the one measured with the thermocouple. At higher temperatures, in particular around the rotational ordering phase-transition temperature (260 K), no heating by the laser pulse was detected.

III. EXPERIMENTAL RESULTS

In Fig. 1, the SH intensity measured at various temperatures is shown as a function of the fundamental photon frequency ($\hbar\omega$). Around room temperature we observe the resonance at about 1.8 eV, previously reported.[8,9] Notice for decreasing temperature the strong enhancement of the SH intensity, the overall blueshift, and the temperature dependence in the line shape of the resonance. Figures 2(a) and 2(b) show the temperature dependence of the zeroth and first moment of the spectrum corresponding to the integrated intensity and to the mean frequency, respectively. In both cases we see a strong temperature dependence at the phase-transition temperature of 260 K. It is also just below this temperature that we observe a splitting of the resonance into two peaks with an intensity ratio of about 3:1. The splitting is about 40 meV. The total width of the signal at the base of the line is approximately 100 meV, which is very large for an exciton bandwidth of a molecular crystal, as discussed below.

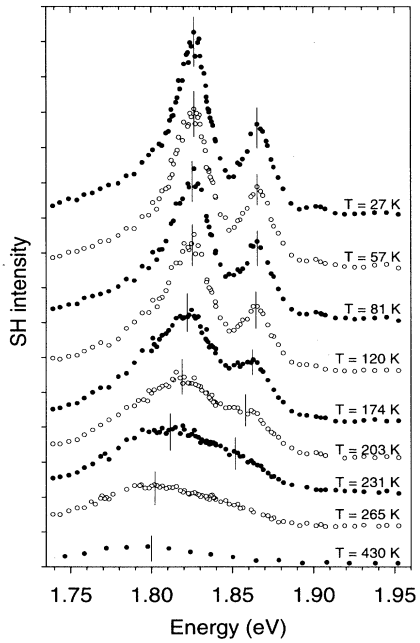

FIG. 1. The temperature-dependent SHG of C_{60} thin films using an m-p polarization combination. The (low) temperatures are not corrected for the heat induced by the laser.

IV. DISCUSSION

Looking at the data in Figs. 1 and 2, there are three main features to be explained: (i) the splitting of the signal below the phase transition; (ii) the linewidth larger than expected for an electric-dipole-forbidden transition in a molecular crystal; and (iii) the overall strong temperature dependence of the SH intensity and line shape.

We propose three possible mechanisms for the splitting, namely, a Jahn-Teller effect, a Davydov splitting,

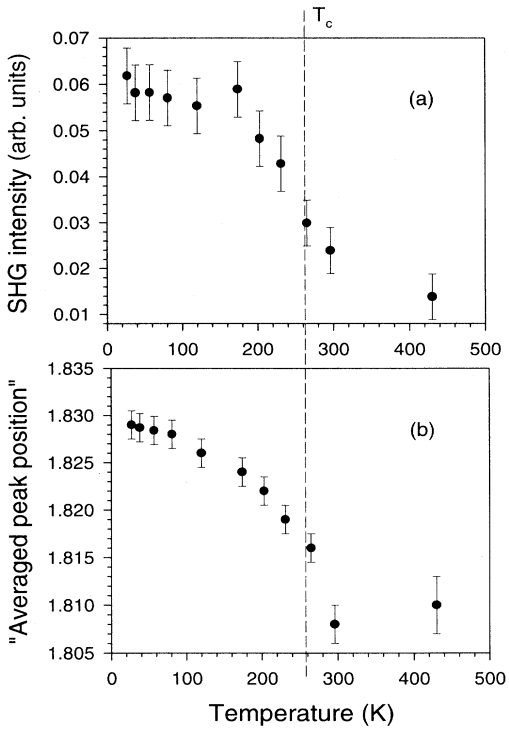

FIG. 2. The temperature dependence of (a) the zeroth moment of the SHG spectrum corresponding to the total intensity and of (b) the first moment corresponding to the mean frequency ("averaged peak position"). Notice that the strongest temperature dependence is at the phase-transition temperature of 260 K (T_c).

and a mixing of the electronic molecular states. A *Jahn-Teller splitting* can probably be discarded since it is expected to be at most 12 meV for the singlet states as determined by Wang *et al.*[12] Before discussing the other two possibilities, we briefly review the basic ideas involving the propagation of excitations and their observation by SHG.

For a schematic picture of the double-resonant SHG process observed in this energy range, we refer to Fig. 1 of Ref. 8. The three-level diagram consists of a magnetic dipole transition from the molecular ground state to the $^1T_{1g}$ excited state (involving a $h_u \rightarrow t_{1u}$ single-electron transition), followed by an electric dipole transition to a $^1T_{1u}$ state at about 3.6 eV ($h_g \rightarrow h_u$), and finally an electric dipole transition back to the ground state ($t_{1u} \rightarrow h_g$). Linear optical experiments exhibit a strong electric-dipole-allowed transition at 3.56 eV with a half width at half maximum of 0.23 eV. Since this width is much larger than the one observed in our experiment (0.06 eV), we concluded that the sharp features in the SHG spectrum must be related to the intermediate $^1T_{1g}$ exciton state.[13,14] This difference in width can easily be understood by comparing the intramolecular excitations, where the electron and the hole are bound, with the intermolecular electron-hole excitations. The latter determine the conductivity gap involving dissociated electron-hole states. As measured by photoconductivity,[15] or by combined photoelectron and inverse-photoelectron spectroscopy,[2] this gap is 2.3 eV. In Fig. 3 we show the energy-level scheme of the intramolecular excitonic excitations (on the left-hand side) and the solid-state intermolecular band-gap excitations (on the right-hand side). The molecular $^1T_{1u}$ state at 3.6 eV is well inside the intermolecular electron-hole continuum and will decay into this with a hopping integral

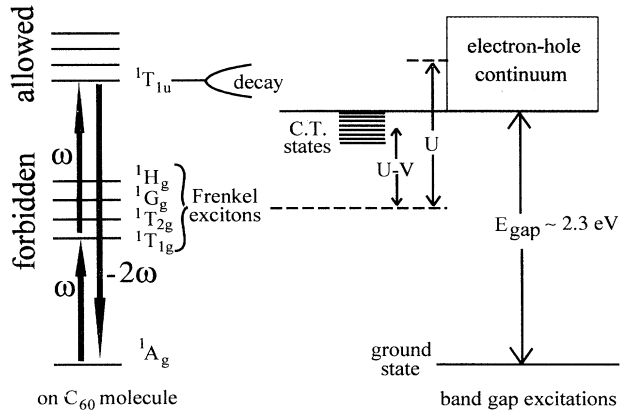

FIG. 3. Part of the singlet excitation spectrum of C_{60} with, on the left side, the intramolecular (on the C_{60} molecule) excitations and, on the right side, the solid-state interband excitations. The multiplet splitting of the optically forbidden HOMO $\rightarrow$ LUMO excitations (Refs. 13 and 14) have an energy lower than the conductivity gap of 2.3 eV and are therefore Frenkel excitons. The (broad) arrows at the left show the three-level diagram responsible for the 1.81-eV SHG resonance. The Frenkel excitons can propagate via the nearest-neighbor charge-transfer (CT) states, which are $U - V$ higher in energy [see Eq. (1)] (Refs. 17 and 18).

comparable to the one-electron (-hole) bandwidth. The $^1T_{1g}$, however, is an electron-hole bound state, inside the band gap, and will therefore have a long lifetime. The extra energy required to dissociate the electron-hole pair of the exciton (i.e., the exciton binding energy) is directly related to the on-site Coulomb interaction measured to be about 1.3 – 1.6 eV by Lof *et al.*[2] Since the $^1T_{1g}$ exciton is bound and the transition to the ground state is electric dipole forbidden, we expect it to be very long lived and we would expect a very small exciton dispersion by conventional optical dipole – optical dipole intermolecular propagation. The still quite large total width of more than 100 meV is therefore difficult to understand in the limit of a molecular solid. It is, however, well known that band-structure effects in C_{60} are not negligible. Lof *et al.*[2] have already suggested a propagation mechanism which could lead to a substantial exciton dispersion. A similar mechanism involving virtual charge-transfer states was previously suggested by Choi *et al.*[16] to explain the dispersional width of optically forbidden excitons in molecular crystals.

This propagation mechanism is shown pictorially in Fig. 4 which demonstrates how an electron-hole pair on site i can propagate to a neighboring site j via a virtual excited intermediate state. This intermediate nearest-neighbor (charge-transfer) state, in which the electron is on site i and the hole on a nearest-neighbor site j (or vice versa), is at an energy $U - V$ (the difference between the on-site Coulomb interaction and the nearest-neighbor Coulomb repulsion[17,18]) higher than the exciton ground-state energy. The net effective exciton hopping integral is given from perturbation theory by

$$T^{\text{exciton}} = \frac{2t_e t_h}{U - V} \tag{1}$$

where $t_{e(h)}$ are the average single electron (hole) nearest-neighbor hopping integrals. It should be noticed that the same electron and hole hopping integrals are involved for the redshift of an exciton energy in the solid relative to the corresponding one in the gas phase. The redshift is then given in first perturbation theory by

$$\Delta E = K\left(\frac{t_e^2 + t_h^2}{U - V}\right), \tag{2}$$

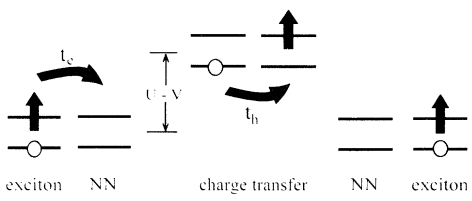

FIG. 4. Schematic representation for the propagation of an exciton via a charge-transfer-mediated mechanism; the electron hops with a one-electron hopping integral (t_e) to its nearest neighbor (NN). This virtual charge-transfer state is at an energy $U - V$ (Refs. 17 and 18) higher than the exciton state. The hole then follows the electron and the whole exciton has moved to the nearest-neighbor position.

where K is a geometrical factor related to the symmetry of orbitals and the nearest-neighbor coordination number. As an example, one has $K = 12$ for a totally symmetrical one-electron and one-hole orbital in a fcc lattice.[19] To estimate the redshift of the $^1T_{1g}$ state, we look at the isolated C_{60} molecule where Gasyna *et al.*[20] found the $^1T_{1g}$ at about 1.92 eV. The same value has been assigned to the $^1T_{1g}$ state by Negri, Orlandi, and Zerbetto[21] using the absorption spectra of C_{60} in the n-hexane solution of Leach *et al.*[22] Koopmans *et al.* found the $^1T_{1g}$ in solid C_{60} resonant at 1.81 eV. This means that in the solid state this exciton is redshifted by 110 meV, which is in the same order as the exciton bandwidth. This supports the above-mentioned exciton hopping mechanism. Detailed calculations of the one-electron (-hole) hopping integrals (discussed further on) show that only nearest-neighbor hopping has to be considered.[10] Therefore, this exciton hopping mechanism does not destroy the molecular Frenkel character of the exciton.

The above-described mechanism for the dispersion of a Frenkel exciton is analogous to the charge-transfer mechanism proposed by Lof *et al.*[2] and to the mechanism originally used to describe excitons in molecular charge-transfer salts.[16] It is also very similar to the so-called superexchange mechanism used to describe Frenkel d-d excitons in $3d$ transition-metal compounds.[23,24]

Assuming that the exciton bandwidth is primarily due to such a dispersional width we look again at the temperature dependence of the line shape. First of all, we might have expected to see only the zero quasimomentum ($\mathbf{k} = 0$) exciton because of the long optical wavelength. At high temperatures, however, the molecules are rapidly rotating, resulting in dynamic orientational disorder which will cause a breakdown of the translational lattice symmetry and of the $\Delta\mathbf{k} = 0$ selection rule. In the extreme case, we would expect to see just the total exciton density of states, as we believe is indeed the case at high temperatures.

Upon lowering the temperature below the phase transition at 260 K, the rotations are strongly reduced, leading to a decrease of dynamic disorder and therefore to approach the $\Delta\mathbf{k} = 0$ selection rule. Since $\mathbf{k}$ then becomes a good quantum number, we will see only the exciton states with $\mathbf{k}$ vectors close to Γ, the center of the Brillouin zone.

In the low-temperature phase there are four molecules per unit cell, so that the exciton band at the Γ point can split up into two or more bands. This splitting, called the *Davydov splitting*, which represents a first possible explanation, will be of the order of the exciton bandwidth and is prominently due to the dependence of the exciton transfer integral on the relative orientation of neighboring molecules.

Recent two-photon excitation of a C_{60} single crystal at 4 K by Muccini *et al.*[25] shows a band at 1.846 eV which is assigned to the same lowest forbidden Frenkel exciton of $^1T_{1g}$ symmetry as discussed in this paper. They also find a second band at higher energy (1.873 eV). They discuss this second band in terms of a crystal-field effect and as a possible Davydov splitting. They give an alternative assignment of the second band as being due to a second forbidden electronic state. Indeed semiempirical quantum-chemical calculations[21] have shown that there are several closely spaced forbidden states which lie in a narrow energy range.[25] The two-photon spectrum of Muccini *et al.* strongly resembles the low-temperature SH resonance in Fig. 1. However, their two-photon absorption, being a third-order nonlinear optical experiment, involves other selection rules than our SHG experiment.

In order to get a more detailed understanding of the results, we carried out the full exciton calculation starting from the basic ideas described by Eqs. (1) and (2). The details will be published elsewhere.[10] Here we restrict ourselves to briefly describe the ingredients of the calculations and the results. In the full calculation the orbital degeneracy of the t_{1u} (threefold) and h_u (fivefold) must be taken into account so that there are several electron and hole hopping integrals depending on the orbital quantum numbers. Satpathy *et al.*[11] have described how those can be obtained from one-particle band-structure calculations using a tight-binding fit. The electron and hole hopping integrals are a function of the relative orientation of the C_{60} molecules. These integrals are completely determined from a single fit to the band structure for a particular given structure. Also we must take into account the multiplet structure of the molecular excitations due to the intramolecular Coulomb interaction as described by Negri, Orlandi, and Zerbetto. These multiplet splittings are not very well known but can be obtained from optical or electron energy-loss data of the gas phase or in solution. The effective exciton transfer integrals are then a sum of products of electron and hole transfer integrals divided by $U - V$. The degree to which each of the electron and hole hopping integrals contribute to the dispersion of a particular exciton is determined by the weight of the electron-hole product function in the particular excitonic state under consideration. In addition to the broadening of the molecular multiplets into bands, there is also a mixing of the various molecular exciton states because of the lowering of symmetry in the crystal.

The only remaining parameters are $U - V$ and the molecular multiplet splitting. Concerning $U - V$ a rough estimate can be taken from the Auger data of Brühwiler *et al.*:[17] $U \simeq 1.1$ eV (0.2 eV is substracted because of the higher exciton energy of a singlet), and $V \simeq 0.7$ eV. This leaves us with $U - V \simeq 0.35 \pm 0.2$ eV. An independent estimate for $U - V$ can also be obtained from the experimental redshift as given in Eq. (2). Taking $U - V = 0.35$ eV, we get a calculated redshift comparable to the experimentally observed one. Concerning the multiplet splitting, we will see below that all we need for the present purpose is a small $^1T_{1g}$ - ^1G_g splitting.

These exciton dispersion calculations show that the $^1T_{1g}$ band at the Γ point splits up into three ^1T_g bands, one ^1A_g and one ^1E_g band [Fig. 5(a)].[10] This can be expected from group theoretical arguments because of the transition from the space group $Fm\bar{3}m$ of the high-temperature phase to the space group $Pa\bar{3}$ of the low-temperature phase.[26,27] The Davydov splitting is found to be about 30 meV, which is close to the experimental splitting (40 meV) of the two peaks. The calcula-

tion, however, predicts that more than 90% of the weight would be in the lowest ^1T_g band. This is inconsistent with our data. Another possible explanation appears when all molecular multiplet states and their mixing are included.

As already mentioned, the quantum-chemical calculations of Negri, Orlandi, and Zerbetto[21] show that the $^1T_{2g}$ and ^1G_g states (in terms of states of isolated C_{60} molecules with icosahedral symmetry) are nearly degenerated with the $^1T_{1g}$. In the crystal, however, the point-group symmetry is lower. This gives rise to a mixing of the icosahedral electronic eigenstates (compare with Table VIII of Ref. 27). When this *mixing* of the $^1T_{1g}$ and ^1G_g Bloch states is taken into account in the exciton dispersion calculations,[10] a second somewhat smaller peak arises at higher energy. This is another possible explanation for the splitting. Accordingly, the main peak at 1.826 eV is (in terms of molecular states) a mixed state of $^1T_{1g}$ with some ^1G_g character, and the second peak at 1.866 eV is a ^1G_g state with some $^1T_{1g}$ character. Since in our SHG experiment we probe the magnetic-dipole-allowed transitions,[28] only the $^1T_{1g}$ component is visible. This would explain the difference in intensity. Figure 5 shows the calculated spectrum with and without mixing of the ^1G_g state. The "mixed" curve agrees well with the experimental data (at the lowest temperature).

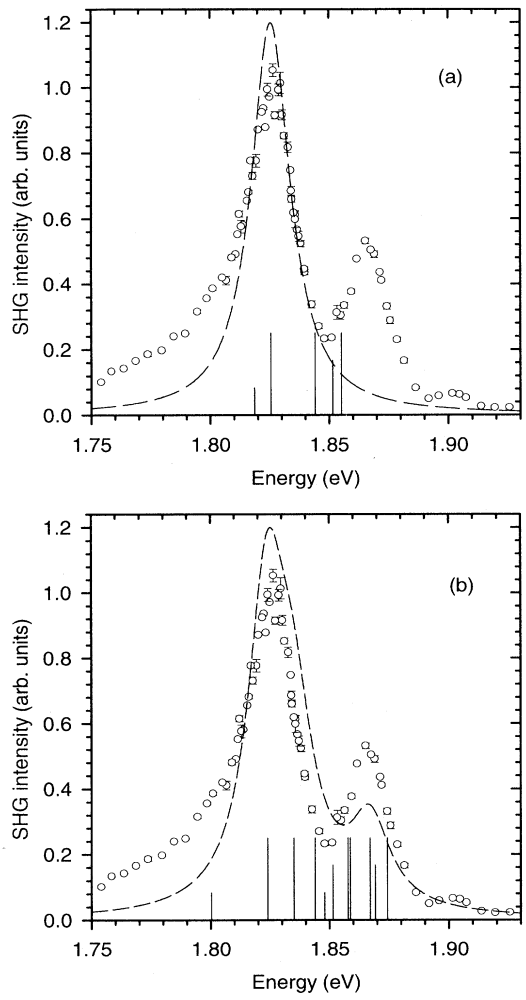

FIG. 5. Comparison of the SHG data taken at the lowest temperature (27 K) with the theoretical calculations for the low-temperature phase ($Pa\bar{3}$). The energy of the $^1T_{1g}$ state of the free C_{60} molecule is taken to be 1.915 eV. The ^1G_g state is taken to be at $+\infty$ (a) or degenerate with the $^1T_{1g}$ (b). The values of $U-V$ are 0.3 eV (a) and 0.35 eV (b). The bars represent the bands at the Γ point; their length corresponds to the degeneracy of the band, threefold (^1T_g), twofold (^1E_g), and nondegenerate (^1A_g).

Although the $^1T_{2g}$ state is also very close to the $^1T_{1g}$, the calculations show that these do not mix, because the neighboring molecules do not have the required orientation for allowing a mixing of the corresponding electronic orbitals. Notice that for the $^1T_{1g}$ and ^1G_g mixing, the same exciton transfer integrals are involved as in the case of a Davydov splitting. Because of these exciton hopping integrals, described by Eq. (1), such a large Davydov splitting (compared to common molecular crystals where an electric-dipole-forbidden transition is considered) and a $^1T_{1g}$ and ^1G_g mixing are possible.

The blueshift of the first moment of the SHG spectrum [Fig. 2(b)] for decreasing temperature most probably has its origin in the orientational ordering, which takes place at the phase-transition temperature (260 K). In the low-temperature phase (T < 260 K), the C_{60} molecules can only jump between two equilibrium positions, and at T < 100 K they are practically frozen in, whereas in the high-temperature phase (T > 260 K), the C_{60} molecules rotate freely in all directions.[29,30] Calculations of the electron (hole) transfer integrals for both phases show that the hopping integrals for the high-temperature phase are larger than those for the low-temperature phase. This means that in the low-temperature phase, where a double carbon-carbon bond faces a pentagon or hexagon, the exciton propagation is less favorable, resulting in a narrowing of the band. Since we are probing the ^1T_g state, which forms the bottom of the band, a narrowing of the band gives rise to a blueshift of the ^1T_g state. The difference in magnitude of the low- and high-temperature hopping integrals has its impact on still another process. Equation (2) gives the relation between the electron (hole) hopping integrals and the redshift of a state in the solid compared to the gas phase. Thus, we expect that at low temperature (where the hopping integrals are smaller than those for the high-temperature phase), the $^1T_{1g}$ state is less redshifted than at high temperature. This also results in a blueshift. Calculations, however, show that the first process will be dominant in our observed blueshift.

What about the strong temperature dependence of the SH intensity? This can also be explained in terms of the dynamic rotational disorder. SHG depends strongly on the retention of coherence in the $^1T_{1g}$ intermediate exciton state in a time scale determined by the excitation transition matrix elements. The intensity of the SHG goes like $(N_{\mathrm{coh}})^2$, where N_{coh} is the number of molecules coherently (in phase) contributing to the signal. Rotational motion during excitation results in dephasing of true oscillators so that N_{coh} is expected to decrease strongly with temperature. This is a so-called T_2 (i.e., dephasing time) like relaxation process. One expects,

therefore, a strong dephasing if the rotation time of a C_{60} molecule is of the same order as the time between the first and second transition. We estimate the time of revolution for a freely rotating C_{60} molecule at temperature T as $\tau_{\rm rot} = 2\pi\sqrt{I/2k_BT}$, where $I{=}1{\times}10^{-43}$ kg m^2 is the moment of inertia of the molecule. Since the rotation axes and angular velocity of neighboring C_{60} molecules are uncorrelated, the rotational motion during the lifetime of the intermediate state leads to a stochastic dephasing of the wave function on the individual molecules. An estimate for the time between the magnetic dipole transition and the first electric dipole transition by Fermi's golden rule gives $\tau^{-1} \simeq r_{\rm ball}^2 G\rho_{\rm final}$, where $r_{\rm ball}^2$ is the radius of the C_{60} molecule, G is the energy current of the laser pulse and $\rho_{\rm final}$ is the density of states of the final states (with one electron in the t_{1u}, the lowest unoccupied molecular orbital (LUMO), and one hole in the h_g, the second highest occupied molecular orbital (HOMO -1)). We choose $\rho_{\rm final} = W^{-1}$, where $W \sim 0.5$ eV is the bandwidth of LUMO or HOMO $-$ 1. At $T = 300$ K we find $\tau_{\rm rot} \simeq \tau \simeq 10^{-11}$ s. This means that, in the time spent between the first and second transition, a given C_{60} molecule can perform a full rotation. Since the rotation of the different molecules is uncorrelated, this leads to strong (T_2) dephasing and decreasing of the SH intensity. We note, however, that electron-phonon interactions can play a similar role in the observed temperature dependence. A strong temperature dependence of the intensity can also be found in photoluminescence experiments. There, the increase in intensity occurs at a somewhat lower temperature compared with the phase transition and the interpretation is still controversial.[31–35]

Liu *et al.* have also done temperature-dependent SHG of C_{60} films, and they also observe a jump in the SH intensity around the orientational phase transition.[36] Their increase of the SH intensity for decreasing temperature is much less than what we observe. That is probably because they have done the SHG experiment using a fixed frequency (1064 nm) which involves other transitions well off the double resonance as found by Wilk *et al.*[37] Their SH intensity might also contain a change due to a shift of the exciton states on going through the phase-transition temperature of 260 K as we have described above.

V. CONCLUSIONS

We have studied the dynamics of the $^1T_{1g}$ Frenkel exciton at $\hbar\omega = 1.81$ eV with temperature-dependent SHG. We find a very strong temperature dependence of this double resonance. Its SH intensity increases strongly close to the phase transition down to about 200 K. We explain this by correlating the rotational disorder of the C_{60} molecules to a T_2 dephasing mechanism. Below the rotational ordering phase transition the SH resonance splits into two bands. Several ideas about what could be the cause of this splitting are discussed. Detailed exciton dispersion calculations taking into account the full symmetry, multiplet structure, and crystal structure, yield large exciton dispersions with total bandwidths of about 100 meV and a Davydov splitting of the $^1T_{1g}$ state of 30 meV. The corresponding SH intensity is calculated to be concentrated to more than 90% in the lowest Davydov component and this is not the observed behavior. The experimental data including the two-component structure in the low-temperature phase are, however, very well described by the theory if the full multiplet structure and mixing of the $^1T_{1g}$ and ^1G_g states due to the lowering of space-group symmetry is included. The experimental data together with the theory support strongly the ideas that the excitons in solid C_{60} are Frenkel like but propagate via virtually excited charge-transfer states described by Lof *et al.*[2] This model is consistent with the total width, the splitting below the phase transition, the redshift relative to the gas phase, and the blueshift with the lowering temperature of the $^1T_{1g}$ exciton state component measured in our SHG experiment.

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